

Efficient method to calculate total energies of large nanoclusters

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We present an approach to calculate total energies of nanoclusters based on first principles estimates. For very large clusters the total energy can be separated into surface, edge and corner energies, in addition to bulk contributions. Using this separation and estimating these with direct, first principles calculations, together with the relevant chemical potentials, we have calculated the total energies of Cu and CdSe tetrahedrons containing a large number of atoms. In our work we consider polyhedral clusters so that in addition our work provides direct information on relaxation. For Cu the effects are very small and the clusters vary uniformly from very small to very large sizes. For CdSe there are important variations in surface and edge structures for specific sizes; nevertheless, the approach can be used to extrapolate to large non-stoichiometric clusters with polar surfaces.

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I. INTRODUCTION

Nanoscience provides an ideal platform in the search for novel materials with desirable and tunable properties. Nanocrystals (NCs) of various sizes and shapes have been found to exhibit a wide variety of physical and chemical properties^{1,2,3,4}, rarely seen in bulk materials. Synthesizing nanoparticles of a given size and shape is notoriously difficult and has become a key focus area due to technically significant properties that depend on the size/shape of the cluster. Growth of such clusters is governed by both kinetics and thermodynamics⁵. If a NC has a highly symmetric crystal structure (such as zincblende), it is likely that when synthesizing, the crystal will grow with no preferred direction of growth. On the other hand, if the crystal structure has a preferred axis of symmetry, as in the hexagonal wurtzite structure which has a unique polar axis, preferential growth along this axis can be expected^{6,7}. Energies associated with various facets (i.e., with different surface orientations) will also play a key role during growth. The total energy, which depends on these facet orientations, will determine the stability of a nanocluster having a given size and shape^{8,9,10}. Calculating these energies associated with large nanocrystals is a nontrivial task. Traditional “brute force” or direct first principles methods become quite laborious as the size of the cluster increases.

First principles methods have provided reliable total energies for atoms and molecules; this is also true in solids, provided that the number of atoms in a given unit cell is relatively small. When this number becomes large (say more than a thousand), then it becomes computationally prohibitive to carry out first principles calculations. Naturally, it is desirable to develop alternate techniques to obtain quality total energies of systems containing a large number of atoms. This work is focused on obtaining such total energy estimates using first principles

values calculated for a small number of well defined clusters. This approach provides crucial information needed to treat accurately these clusters as well as general results that can be used for other classes of clusters.

II. METHODOLOGY

A. Computational method for clusters

Surface energies have been extracted from first principles slab (total energy) calculations by several groups (see for example, Refs.^{11,12}). Besides that, a first principles wedge-shaped approach has also been proposed to calculate the surface energies of polar surfaces¹⁰. In the present work, our goal is somewhat different compared to the above. We will use energies obtained from first principles calculations on polyhedral nanoclusters to estimate total energies of larger nanoclusters. The energy can be written as

$$E_{tot}^{poly} = \sum_{\alpha} \sigma_{\alpha} A_{\alpha} + \sum_{\beta} \epsilon_{\beta} L_{\beta} + \sum_{\gamma} c_{\gamma} + \sum_i N_i \mu_i, \quad (1)$$

where, σ_{α} , ϵ_{β} and c_{γ} denote surface, edge and corner energies respectively, N_i is the number of atoms of type i , and μ_i is the corresponding chemical potential. The last term in Eq. (1) contains the bulk energy if the chemical potentials satisfy the conditions given in section II B. For a stoichiometric cluster the total energy is independent of the individual chemical potentials and is well-defined relative to the energy of the bulk crystal.

In the present work, a least-squares fit for the total energies of several small clusters were used to estimate the surface, edge and corner energies (as parameters). If the above energies can be evaluated in a computationally efficient way, then the total energy of a cluster (polyhedron), containing a (substantially) large number

of atoms, can be expressed *algebraically* as in Eq. (1). We demonstrate that using accurate density functional theory (DFT) based estimates of total energies of a few small clusters, it is possible to estimate the above (surface, edge, corner) contributions (as well as chemical potentials) and then use them (as parameters) in larger clusters to estimate total energies. The calculations were based on the local density approximation within the DFT¹³ as implemented in the local orbital SIESTA code¹⁴. Norm-conserving nonlocal pseudopotentials of the Troullier-Martins type¹⁵ were used to describe all the elements.

For a specific shape, the cluster can be defined by one characteristic length ℓL_0 , so that the surface and edge terms can be expressed as $A_\alpha = a_\alpha \ell^2$, $L_\beta = b_\beta \ell^1$ respectively, with a_α and b_β being constants. Therefore, Eq. (1) may be written in the following form;

$$\begin{aligned} & (E_{tot}^{poly} - \sum_i N_i \mu_i) / \ell^2 \\ &= \sum_\alpha \sigma_\alpha a_\alpha + \sum_\beta \epsilon_\beta b_\beta / \ell + \sum_\gamma c_\gamma / \ell^2. \end{aligned} \quad (2)$$

We label the energy expression on the left side of Eq. (2) as “termination energy” since it is the added energy due to the presence of surfaces, edges and corners. For example, for a tetrahedral structure bounded by four (111) surfaces. (see Fig. 1), The characteristic size is ℓL_0 (ℓ being an integer and L_0 the nearest neighbor distance along an edge), representing an edge of a triangular (111) facet. The tetrahedral structure includes four equivalent (111) surfaces, six equivalent (111) – (111) edges, and four equivalent (111) – (111) – (111) corners. This choice enables us to work with well defined (111) surfaces, as well as equivalent corners, edges and surfaces. In this case, the termination energy in Eq. (2) turns out to be

$$(E_{tot}^{poly} - \sum_i N_i \mu_i) / \ell^2 = \sqrt{3} \sigma L_0^2 + 6 \epsilon L_0 \frac{1}{\ell} + 4c \frac{1}{\ell^2}. \quad (3)$$

In later discussions, we use the above equation for both FCC Cu clusters and zincblende CdSe clusters.

B. Non-stoichiometric case

One of the examples we have chosen to study is the binary compound CdSe. When the cluster is stoichiometric, the number of Cd atoms will be equal to the number of Se atoms, and the sum of the chemical potentials, $\mu_{Cd} + \mu_{Se}$ = total energy per CdSe pair, can easily be evaluated from bulk total energy calculations. In a non-stoichiometric case, the number of Cd atoms is different from the number of Se atoms, and some energy terms, such as the surface energies, depend on the separate values of μ_{Cd} or μ_{Se} , instead of their sum. To examine this further, we set lower and upper bounds for the individual chemical potentials (pertaining to bulk CdSe) as

$$\begin{aligned} E_{tot}^{bulk}(CdSe) &= \mu_{Cd} + \mu_{Se} \\ &= E_{tot}^{bulk}(Cd) + E_{tot}^{bulk}(Se) + \Delta H_f, \end{aligned} \quad (4)$$

where ΔH_f is the formation energy. The bulk values, $E_{tot}^{bulk}(Cd)$ and $E_{tot}^{bulk}(Se)$, are obtained from total energy calculations of pure Cd and pure Se (per atom, in their equilibrium structures) separately, while $E_{tot}^{bulk}(CdSe)$ is the total energy of a CdSe pair in the bulk.

Following well known procedures¹³, we can set bounds listed below for the chemical potentials of the individual species in CdSe:

$$E_{tot}^{bulk}(Cd) + \Delta H_f \leq \mu_{Cd} \leq E_{tot}^{bulk}(Cd) \quad (6)$$

$$E_{tot}^{bulk}(Se) + \Delta H_f \leq \mu_{Se} \leq E_{tot}^{bulk}(Se). \quad (7)$$

The right hand side of the first inequality represents the fact that, μ_{Cd} in the cluster must be smaller than the (pure Cd) bulk value $E_{tot}^{bulk}(Cd)$, since otherwise, Cd must phase separate. The left hand side of this inequality follows from the fact that for μ_{Se} , one can use the same argument and utilize Eq. (5) to obtain the following:

$$0 \leq -\mu_{Se} + E_{tot}^{bulk}(Se) = \mu_{Cd} - E_{tot}^{bulk}(Cd) - \Delta H_f. \quad (8)$$

From the above arguments, it appears that we can only evaluate the individual chemical potentials, μ_{Cd} and μ_{Se} , within the range given above. However, for a specific family of non-stoichiometric clusters having the same shape, we demonstrate below that the total energy can be determined with no knowledge of the chemical potentials.

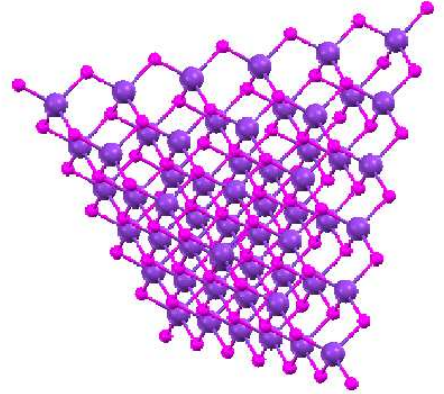


FIG. 1: CdSe Zincblende (tetrahedral) structure bounded by four (111) surfaces terminated by Cd atoms. Small dots represent Cd atoms, while large dots represent Se atoms. The characteristic size is ℓL_0 (ℓ being an integer, with $\ell = 6$ shown here), representing an edge of a triangular (111) facet.

We first show that the total energy of any CdSe (zincblende) tetrahedron, E_{tot}^{poly} , bounded by similar (111) facets as shown in Fig. 1, can be expressed in a slightly different form of Eq. (1), i.e.,

$$\begin{aligned} & E_{tot}^{poly}(CdSe) - N_{Cd} \mu_{Cd} - N_{Se} \mu_{Se} \\ &= \sqrt{3} \sigma L_0^2 \ell^2 + 6 \epsilon L_0 \ell + 4c. \end{aligned} \quad (9)$$

Here L_0 is the nearest neighbor distance along an edge of the tetrahedron.

Combining with Eq. (4), we obtain:

$$\begin{aligned} E_{tot}^{poly}(CdSe) - N_{Se}E_{tot}^{bulk}(CdSe) \\ = (N_{Cd} - N_{Se})\mu_{Cd} + \sqrt{3}\sigma L_0^2\ell^2 + 6\epsilon L_0\ell + 4c. \end{aligned} \quad (10)$$

However, note that

$$N_{Cd} - N_{Se} = \frac{1}{2}\ell^2 + \frac{3}{2}\ell + 1, \quad (11)$$

which results from a simple count of the atoms in a tetrahedron having an edge of length ℓL_0 (ℓ being an integer and L_0 the nearest neighbor distance along an edge). This result clearly shows that the difference in the number of Cd and Se atoms arises from surfaces (ℓ^2), edges (ℓ^1) or corners (ℓ^0), and leads to the following important simplification:

$$\begin{aligned} E_{tot}^{poly}(CdSe) - N_{Se}E_{tot}^{bulk}(CdSe) \\ = \left(\frac{1}{2}\mu_{Cd} + \sqrt{3}\sigma L_0^2\right)\ell^2 + \left(\frac{3}{2}\mu_{Cd} + 6\epsilon L_0\right)\ell + (\mu_{Cd} + 4c). \end{aligned} \quad (12)$$

The significance of Eq. (12) is that, even in this non-stoichiometric case, it is possible to estimate the total energies independent of the chemical potentials. This is because in the above equation, the coefficients of ℓ^2 , ℓ and the constant term act as straightforward parameters to be estimated. Since there is no volume (L^3) term on the right side of Eq. (12), neither μ_{Cd} nor μ_{Se} will have a direct effect on the final total energy to be predicted. Note that $E_{tot}^{bulk}(CdSe)$ has an unambiguous value, as the total energy per $CdSe$ pair in the (bulk) zincblende structure. Now the parameters, such as surface energy, edge energy, and corner energy, can be fitted using several, known (DFT based) total energy values from small clusters. Finally, in order to predict the total energies of large polyhedrons, the algebraic expression in Eq. (12) can be utilized as previously.

III. RESULTS

Test results from pure (fcc) Cu as well as (zincblende) CdSe clusters show that this scheme is reliable to a high degree of accuracy. One of the significant results of the present study is our ability to calculate energies of nanoclusters that are non-stoichiometric and that have polar surfaces. Furthermore, we will demonstrate that the total energies can be evaluated independently of individual chemical potentials (Eq. (6) (7)).

A. FCC Cu

We begin our discussion with pure fcc Cu clusters, which are regular tetrahedral clusters having a characteristic length, $L = \ell L_0$ (ℓ being a positive integer,

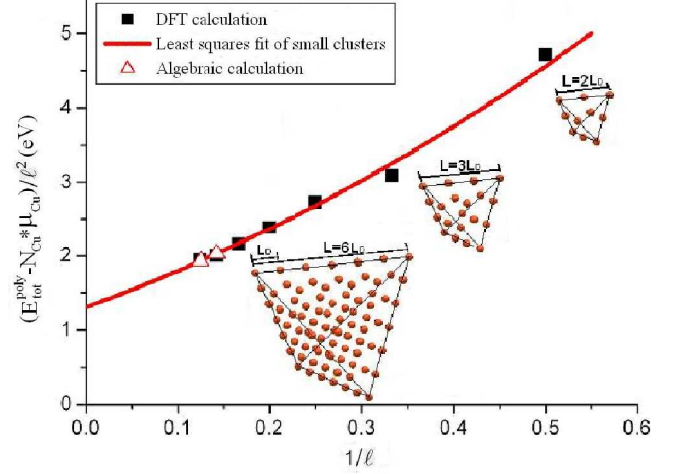


FIG. 2: The termination energy (see text for definition) contribution scaled by ℓ^2 for Cu clusters as a function of the inverse of the characteristic size ($1/\ell$) of the tetrahedrons. Y-intercept is proportional to surface energy(σ), slope is proportional to edge energy(ϵ), and curvature is proportional to corner energy(c). The solid squares represent the values calculated using DFT while the open triangles represent the estimated values from our algebraic expression. The solid line is a least squares fit for the DFT points.

$L_0 = 2.545\text{\AA}$ after geometric relaxation), bounded by four, equivalent (111) facets. The relevant chemical potential, μ_{Cu} , can be obtained from a fcc bulk total energy calculation. The first principles total energies, E_{tot}^{poly} , for the tetrahedrons are obtained after fully relaxing a given cluster.

We find it is more useful to focus on the energy term ($E_{tot}^{poly} - N_{Cu}\mu_{Cu}$), since this represents a termination energy to the bulk chemical potential contribution due to the presence of surfaces, edges and corners. The termination energies scaled by the square of a characteristic length ℓ^2 , i.e., $(E_{tot}^{poly} - N_{Cu}\mu_{Cu})/\ell^2$, for different sized clusters ($\ell = 2$ to $\ell = 8$) calculated using DFT are shown as solid squares in Fig. 2. To estimate surface, edge and corner energies, total energies of a few small clusters ($\ell = 2, 3, 4, 5, 6$) were used in a least squares fit according to Eq. (3). The estimated σ , ϵ and c were 0.1164 eV/\AA^2 , 0.2949 eV/\AA , and 1.0047 eV respectively. A previous DFT calculation has reported the (111) fcc Cu surface energy $\sigma = 0.1213\text{ eV/\AA}^2$ ¹⁶ while the experimental result for the surface energy of $Cu_{(111)}$ is 0.1144 eV/\AA^2 ¹⁷. Hence our calculated σ value is in good agreement with previous theoretical and experimental values. Using the three parameters for surface, edge and corner energies, we now estimate the termination energy as a function of cluster size, as shown in Fig. 2. The estimated total energies for the two larger clusters ($\ell = 7$ and $\ell = 8$) are carried out using the algebraic expression shown in Eq. (3).

ℓ (L_0)	N_{Cu}	E_{tot}^{poly}/ℓ^2 (eV)	
		DFT	algebraic
2	10	-3041.43	
3	20	-2704.60	
4	35	-2662.65	
5	56	-2726.96	
6	84	-2840.92	
7	120	-2981.98	-2981.95
8	165	-3139.40	-3139.41

TABLE I: Total energies for tetrahedral fcc Cu clusters

The energies predicted using the algebraic expression are in excellent agreement with the ‘exact’ calculations from first principles as evident from the results for $\ell = 7$ and $\ell = 8$ tetrahedrons in Table I and Fig. 2. The above result clearly provides further support for our method of estimation.

B. Tetrahedral, zincblende based CdSe clusters

The second system in our discussion is a non-stoichiometric, zincblende CdSe cluster bounded by four equivalent (111) facets terminated by Cd atoms. As described in the Methodology section and Fig. 1, the characteristic size is ℓL_0 with $L_0 = 4.342\text{\AA}$. The bulk values, $E_{tot}^{bulk}(Cd)$ and $E_{tot}^{bulk}(Se)$, are obtained from total energy calculations of pure Cd (in hcp structure) and pure Se (in trigonal structure) separately, while $E_{tot}^{bulk}(CdSe)$ is the total energy of a CdSe pair (in zincblende structure). Through explicit calculations, we obtain $E_{tot}^{bulk}(Cd) = -1467.17$ eV; $E_{tot}^{bulk}(Se) = -256.97$ eV; $E_{tot}^{bulk}(CdSe) = -1724.84$ eV. Therefore, the formation energy is calculated to be $\Delta H_f = -0.7$ eV (from Eq. (5)).

In Table II, DFT based total energies for polyhedrons from $\ell = 2$ to $\ell = 8$ are shown. Using DFT based small clusters energies (for $\ell = 2, 3, 4, 5, 6$), we have obtained the necessary fitting parameters involving surface energy, edge energy, and corner energy, which vary within the intervals $50 - 61$ meV/ \AA^2 , $227 - 268$ meV/ \AA , and $39 - 214$ meV respectively. We also see that certain clusters undergo noticeable reconstructions, while others do not. Surface energy varies within the interval $50 - 61$ meV/ \AA^2 , showing an average of surface energies within the reconstructed (for example $\ell = 4, 5$) and non-reconstructed (for example $\ell = 6$) structures, which is reasonably lower than previous DFT calculations ($\sigma \sim 75 - 95$ meV/ \AA^2 ¹¹). Surface reconstructions have been studied before using various methods, such as the tight binding method¹⁸. Here we have observed size dependent, surface reconstruction of the CdSe system by using DFT combined with the local density approximation.

In Fig. 3, for different Cd chemical potentials, we plot the scaled termination energy, $(E_{tot}^{poly} - N_{Cd}\mu_{Cd} - N_{Se}\mu_{Se})/\ell^2$ by subtracting the chemical potential con-

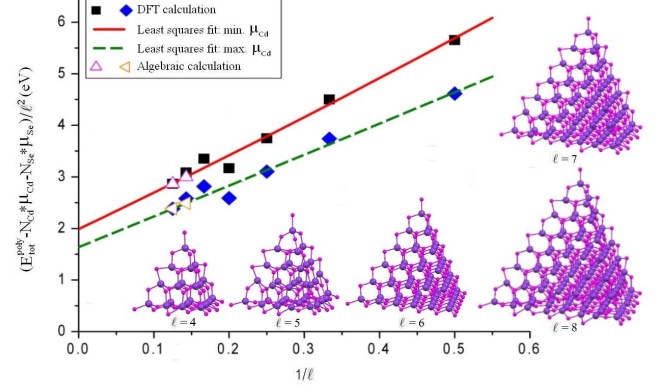


FIG. 3: The termination energy contribution (see text) divided by ℓ^2 for CdSe clusters as a function of the inverse of the characteristic size. The squares correspond to DFT energies while the lines are least squares fits. The solid line corresponds to the minimal μ_{Cd} , while the dashed line corresponds to the maximal μ_{Cd} . The open triangles represent energies obtained from our algebraic calculation after fitting.

tributions from the total energy of the cluster as a function of $1/\ell$. The algebraic values of E_{tot}^{poly} obtained from Eq. (3) for $\ell = 7, 8$, are indicated on the fitted curves, along with other values resulting from direct DFT calculations. In general the termination energy depends on the choice of μ_{Cd} , as evident from Fig. 3, which is required to compare these surfaces with other surfaces. However, the predicted values for the total energy (E_{tot}^{poly}) of the $\ell = 7, 8$ clusters relative to other polyhedra with the same shape can be found using Eq. (10), which yields the same value for different values of μ_{Cd} (see Table II; i.e., the algebraic value $E_{tot}^{poly}/\ell^2 = -4032.30$ eV for the $\ell = 7$ polyhedron for all the values of μ_{Cd} .) This value is comparable to the energy obtained from the direct DFT calculations, which is an advantage since it shows that we can obtain certain energies independent of μ_{Cd} , as discussed earlier.

ℓ (L_0)	N_{Cu}	N_{Se}	E_{tot}^{poly}/ℓ^2 (eV)	
			DFT	algebraic
2	10	4	-3920.98	
3	20	10	-3542.94	
4	35	20	-3528.42	
5	56	35	-3644.61	
6	84	56	-3821.40	
7	120	84	-4032.21	-4032.30
8	165	120	-4263.30	-4263.30

TABLE II: CdSe (zincblende) total energies for various cluster sizes.

IV. DISCUSSION

For polyhedral nanoclusters of fcc Cu, calculations from 10 to 165 atoms show that the energies are well described by this form even for small clusters. Thus the energies for all sizes can be determined efficiently based on calculations for small clusters and we propose that this is a useful approach for metals.

When testing this approach for CdSe polyhedrons that are Cd terminated and non-stoichiometric, one encounters energy contributions that depend on the individual chemical potentials, as seen from Eq. (1) which defines E_{tot}^{poly} . These chemical potentials are subject to upper and lower bounds¹³ (see inequalities (6), (7)). However, it turns out that the total energies of even the non-stoichiometric CdSe polyhedra considered here can be obtained without knowing the individual chemical potentials. This is sufficient to extrapolate to large size for this family of clusters independent of chemical potentials and using only directly calculated total energies. The reason for the above is that the total energy of such clusters can be calculated from well defined bulk energies by adding surface, edge and corner termination terms; these termination terms appear as mere parameters that scale with the dimensions of the cluster and can be estimated from DFT calculations of small clusters with similar topologies. In addition, the surface, edge and corner termination terms can be used for other clusters by including the chemical potentials in the way given in Eq. (12).

For CdSe, we find an overall trend similar to that for Cu; however, there are deviations from a smooth curve for the energies as a function of size. The deviations are likely to be associated with reconstructions that are seen for certain nanocluster sizes. These reconstructions prob-

ably originate from the changes in state occupations near the Fermi energy, with the largest changes apparently occurring for the edges. Also note that as the cluster size $L \rightarrow \infty$, the corner and edge contributions become small compared to the surface energies and thus providing a way of estimating the latter for large clusters.

The total energies are described well by a least squares fit, carried out using the results for 5 clusters with 14 to 140 atoms, which accurately determines the energies for clusters with 204 and 285 atoms. However, the division into three separate contributions as surface, edge and corner energies, is not as well determined due to the (possible reconstruction-induced) variations between the different clusters. The estimated surface energy represents an average of different reconstructed and unreconstructed clusters, which is reasonably lower than the value reported in previous DFT calculations, as pointed out in the results section.

V. CONCLUSION

In summary, we have presented an efficient method for calculating total energy of large nanoclusters using a parametrized, algebraic form with parameters fitted from small, first principles based, nanocluster calculations. The method appears to work quite well for pure metals. Even for non-stoichiometric, semiconducting clusters with polar surfaces, this approach provides a way of estimating total energies of large clusters, important information such as relaxation energies that are specific to the chosen clusters, as well as surface, edge and corner energies that can be used for other clusters.

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